




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |           |   |
|--|-----------|---|
| <b>(51) International Patent Classification <sup>5</sup> :</b><br><b>B01D 71/02, 69/10, B01J 29/00</b>   | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 93/19840</b><br><b>(43) International Publication Date:</b> 14 October 1993 (14.10.93)  |
| <b>(21) International Application Number:</b> PCT/GB93/00627<br><b>(22) International Filing Date:</b> 26 March 1993 (26.03.93)<br><br><b>(30) Priority data:</b><br>9206783.4 27 March 1992 (27.03.92) GB<br><br><b>(71) Applicant (for all designated States except US):</b> THE BRITISH PETROLEUM COMPANY PLC [GB/GB]; British House, 1 Finsbury Circus, London EC2M 7BA (GB).<br><br><b>(72) Inventors; and</b><br><b>(75) Inventors/Applicants (for US only) :</b> BRATTON, Graham, John [GB/GB]; 154 Old Farm Avenue, Sidcup, Kent DA15 8AL (GB). NAYLOR, Timothy, de Villiers [GB/GB]; 10 Kingswood Close, Englefield Green, Egham, Surrey TW20 0NQ (GB). |           | <b>(74) Agent:</b> WILSON, Michael, John; BP International Limited, Patents & Agreements Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).<br><br><b>(81) Designated States:</b> AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).<br><br><b>Published</b><br>With international search report.<br><br> |
| <b>(54) Title:</b> DEPOSITION PROCESS<br><br><b>(57) Abstract</b><br><br>A zeo-type material may be deposited on a porous support to provide a zeolite membrane for separation and/or catalysis, by a process in which before the zeo-type material is crystallized on the support in step (iii), the support has been contacted in step (i) with a solution or suspension of a source of silicic acid to bond oligomers of silicic acid thereonto, and then in step (ii) said support carrying the bonded oligomer and said solution or suspension are separated.   |           |   |

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |                                       |    |                          |
|----|--------------------------|----|---------------------------------------|----|--------------------------|
| AT | Austria                  | FR | France                                | MR | Mauritania               |
| AU | Australia                | GA | Gabon                                 | MW | Malawi                   |
| BB | Barbados                 | GB | United Kingdom                        | NL | Netherlands              |
| BE | Belgium                  | GN | Guinea                                | NO | Norway                   |
| BF | Burkina Faso             | GR | Grèce                                 | NZ | New Zealand              |
| BG | Bulgaria                 | HU | Hungary                               | PL | Poland                   |
| BJ | Benin                    | IE | Ireland                               | PT | Portugal                 |
| BR | Brazil                   | IT | Italy                                 | RO | Romania                  |
| CA | Canada                   | JP | Japan                                 | RU | Russian Federation       |
| CF | Central African Republic | KP | Democratic People's Republic of Korea | SD | Sudan                    |
| CG | Congo                    | KR | Republic of Korea                     | SE | Sweden                   |
| CH | Switzerland              | KZ | Kazakhstan                            | SK | Slovak Republic          |
| CI | Côte d'Ivoire            | LJ | Liechtenstein                         | SN | Senegal                  |
| CM | Cameroon                 | LK | Sri Lanka                             | SU | Soviet Union             |
| CS | Czechoslovakia           | LU | Luxembourg                            | TD | Chad                     |
| CZ | Czech Republic           | MC | Monaco                                | TG | Togo                     |
| DE | Germany                  | MG | Madagascar                            | UA | Ukraine                  |
| DK | Denmark                  | ML | Mali                                  | US | United States of America |
| ES | Spain                    | MN | Mongolia                              | VN | Viet Nam                 |
| FI | Finland                  |    |                                       |    |                          |

DEPOSITION PROCESS

The present invention relates to a deposition process useful in membrane preparation.

Zeolites and related crystalline materials are well known for their ability to accomplish separations and to act as catalysts.

5   Membranes are well known in separations applications, and membranes incorporating zeolites are known. These membranes are of a number of distinct types.

CA 1235684 claims a filter for substance separation, comprising a substrate made of a porous glass and a zeolite-based film formed  
10   directly on the porous glass, the zeolite-based film having a thickness of 1 micron to 500 microns. The filter is prepared by suspending, for example, a borosilicate glass in an aqueous solution of sodium hydroxide and tetrapropylammonium bromide, and heating in an autoclave.

15   JP-A-63291809 describes a membrane comprising a film of zeolite on a porous alumina carrier.

EP-A-180200 describes a membrane comprising a porous support impregnated with fine particles of a zeolite. The membrane is prepared by permeating, for example, an ultrafiltration membrane, or  
20   a porous glass, with an alkaline solution of ultrafine (e.g. less than 75 angstrom diameter) zeolite particles. These particles become lodged in the pores of the support.

EP-A-180200 describes a process for preparing a zeolite membrane in which a zeolite synthesis gel is passed through a  
25   microfilter and deposited in a thin film on the surface of a

support.

DE-A-3827049 describes a zeolite membrane consisting of a layer of zeolitic crystals on a porous support. During preparation of the membrane, the support is provided with a nucleo-active surface by  
5 immersing the porous support for a short time in an alumina-containing solution, and then evaporating the solvent.

Our European patent application No. 91309239 (published as EP-A-481660), whose disclosure is herein incorporated by reference, describes a process for the production of a membrane comprising a  
10 film of a zeo-type material over the pores of a porous support, which comprises immersing at least one surface of a porous support in a synthesis gel which is capable of crystallising to produce a crystalline zeo-type material; inducing crystallisation of said gel so that zeo-type material crystallises on the support; removing the  
15 support from the mix; and repeating these steps one or more times to obtain a membrane in which the zeo-type material is crystallised directly from and bonds directly to the support. It also describes a novel membrane which comprises crystals of a zeo-type material carried by a porous support characterised in that the crystal growth  
20 of the zeo-type material is essentially continuous over the pores of the support and that the zeo-type material is crystallised directly from and bonds directly to the support.

Our European patent application No. 91309237 (published as EP-A-481658), whose disclosure is herein incorporated by reference,  
25 discloses that, when depositing a zeo-type material from a synthesis gel onto a porous support, the use of a support incorporating a defined surface coating produces an enhanced growth of zeo-type material in the initial immersion and crystallisation step; it describes and claims a process for the deposition of a zeo-type  
30 material on a porous support, which comprises immersing at least one surface of the porous support in a synthesis gel which is capable of crystallising to produce a crystalline zeo-type material, and inducing crystallisation of said gel so that zeo-type material crystallises on the support, characterised in that said surface of  
35 the support incorporates a surface coating of nickel, cobalt or

molybdenum in the form of the metal and/or the oxide.

We have now found that a particular treatment of a support for a membrane comprising zeo-type material, can improve the process for preparing the membrane.

5       Accordingly, the present invention provides a process for the deposition of a zeo-type material on a porous support, which comprises the following steps: i) contacting at least one surface of the porous support with a solution or suspension containing a source of silicic acid, under conditions such that oligomers of silicic  
10       acid become bonded directly to said surface of the support; ii) separating the support with said oligomers bonded thereto and said solution or suspension containing a source of silicic acid; and iii) subsequently contacting said surface of the support with a synthesis gel which is capable of crystallising to produce a crystalline  
15       zeo-type material, and inducing crystallisation of said gel so that zeo-type material crystallises on said surface.

      Suitable solutions or suspensions containing a source of silicic acid include basic mixtures of silica or a silicate with a solvent or suspending medium; such mixtures may contain a silicate,  
20       e.g. sodium silicate already containing silicic acid oligomers or these may form slowly. Preferably, however, there is used a synthesis gel which is capable of producing a crystalline zeo-type material. Such gels contain a source of silicic acid as well as other components. When such a gel is used in step i) of the process  
25       of the invention, this gel may be of the same composition as the gel used in step iii) of the process, or it may be of a different composition. Preferably it is of the same composition. Any of the synthesis gels described below as being suitable for use in step  
30       iii) of the process of the invention may be used in step i) of the process of the invention.

      The contact of surface of the support in step (i) with the solution or suspension preferably involves immersion of the surface of the support therein, but other methods may be used, such as application of a layer thereof, e.g. by painting on the surface, and  
35       maintenance of that layer of solution or suspension in contact with

the surface until the silicic acid oligomers have bonded to it; the contact is maintained with the liquid, so that the humidity level above the surface is kept high enough, e.g. by operation under autogenous pressure, to avoid the solution or suspension drying on the surface. In step (ii) the surface having the oligomers bonded thereto and the solid/suspension are separated, e.g. by gravity or centrifugal separation; preferably after an immersion in step (i), the support is removed from the solid/suspension, but other methods such as draining or filtration of the solid/suspension therefrom may be used. In step (iii) the contact of surface and the synthesis gel may be by immersion, but other methods may be used such as painting in the manner as in step (iii) as described above but with contact until the zeo-type material has crystallized on the surface.

We have found that, when a porous support is contacted with, e.g. immersed in, such a synthesis gel under conditions which ultimately lead to the formation of crystals of zeo-type material, a number of distinct stages in the deposition process can be identified. The final stage is the deposition of crystalline zeo-type material on the surface of the support. Before that, however, an initial deposit of oligomers of silicic acid is formed on the surface of the support. In the process according to the invention, where the solution or suspension containing a source of silicic acid in step i) is a synthesis gel, the support is removed from the gel at this initial stage, and then recontacted, e.g. reimmersed in a fresh synthesis gel according to step iii) until zeo-type crystals have grown on the surface. Surprisingly, this two-stage contact, e.g. immersion process leads to cover of the zeo-type material on the surface of the porous support which is much greater than when a single immersion leading to crystal deposition is used.

Preferably the support is treated between steps ii) and iii) of the process of the invention, for example by washing with water such as distilled and/or deionized water, to remove any adherent residual solution or suspension from step (i) and/or to remove loose material prior to contact, e.g. immersion in synthesis gel in step

iii). A water jet may be used. The treatment should be vigorous enough to remove loose material but should of course not remove the deposit of oligomers of silicic acid bonded to the surface of the support. After the washing step, the support carrying the oligomer deposit is preferably dried before step (iii), e.g. at 50-120°C such as 80-105°C, for 1-100 minutes such as 5-50 minutes.

Preferably, the porous support is completely immersed in the solution or suspension containing a source of silicic acid, and subsequently in a synthesis gel. Alternatively, if desired, only one surface of the support may be in contact with the solution or suspension and then the gel. This may be useful, for example, if it is desired to produce a membrane in the form of a tube where only the inside or the outside of the tube needs to carry zeo-type material. It may also be useful if it is desired to produce a membrane containing two different zeolites, one on each side of the support. Use of such a bi-functional membrane would be equivalent to using two separate membranes each carrying a different zeolite. It is also of course possible to immerse the support completely in the solution or suspension containing a source of silicic acid, but subsequently to contact only one side of the support with the synthesis gel according to step iii).

The contact, e.g. immersion of the surface of the porous support in a solution or suspension containing a source of silicic acid may be carried out more than once if desired. In this case, the surface is preferably treated to remove loose material after removal from one solution or suspension prior to contact, e.g. immersion in a fresh solution or suspension.

The surface of the porous support must be contacted, e.g. immersed in the solution or suspension containing a source of silicic acid for a period of time such that oligomers of silicic acid become bonded to the surface. The optimum time taken for this contact will of course depend on the nature of the solution or suspension used, and also on the temperature. The temperature of the contact may vary widely, for example from 20 to 200°C; room temperature may be convenient, but this may necessitate a rather

long contact time, whereas contact at a higher temperature will reduce the optimum time. In general, contact, e.g. immersion times of 3 minutes to 48 hours such as from 5 minutes to 24 hours, typically from half an hour to 3 hours, are suitable. Thus in a preferred process the combination of contact, e.g. immersion time and temperature is equivalent to less than 8 hours, e.g. less than 6 hours at 90°C, such as 3 minutes to 5 hours at 90°C, e.g. 3 minutes to 30 minutes, suitably when the source of silicic acid is a synthesis gel and/or with pretreated supports as described below.

When the source of silicic acid is a suspension of synthesis gel, which is capable of crystallizing to produce a crystalline zeo-type material, the contact time is sufficient at the contact temperature to bond the oligomers of silicic acid, but insufficient to deposit said crystalline zeo-type material as an adherent coating. The oligomers of silicic acid are bonded to the surface as an amorphous layer. Their presence on the surface may be seen by transmission or scanning electron microscopy, X-ray analysis or EDAX, either on the support itself or after treatment of the support to dissolve the support and leave the oligomers.

Zeo-type materials are well known, and are often referred to as molecular sieves. They are characterised by having a crystal structure made up of tetrahedra joined together through oxygen atoms to produce an extended network with channels of molecular dimensions. Any zeo-type material may be used in the present invention, depending on the desired use of the finished membrane. Zeolites, or aluminosilicates, are the best known example of zeo-type materials. Any zeolite may be used in the present invention, for example those having LTA, FAU, SOD, MEL, MFI or TON structure types as defined in "Atlas of Zeolite Structure Types", Meier and Olsen, 1987, Polycrystal Book Service, Pittsburg USA. Zeolite ZSM-5 and zeolite A, X and Y may be used. Other zeo-type materials which may be used include metallosilicates in which some or all of the aluminium is replaced by another metal, such as gallium, boron, zinc, iron or titanium, and crystalline silicates having zeolite-type structure, such as silicalites as described in



US 4061724 or Nature, 280, 664-665 (1979).

A further class of zeo-type materials are the crystalline aluminophosphates ("ALPO's"), silicoaluminophosphates ("SAPO's") and other metalloaluminophosphates. Such materials are described for  
5 example in "New Developments in Zeolite Science and Technology", Proceedings of the 7th International Zeolite Conference, Tokyo, 1986, page 103. More recent materials such as ALPO-8, ALPO-54 and MCM-9 may be prepared for example as referred to in Zeolites 9 September 1989, page 436.

10 A membrane is a continuous structure whose length and width are very much greater than its thickness. It is selectively permeable to liquids or gases. Any suitable porous support having the desired physical shape may be used in the process of the present invention; suitable forms include for example flat sheet, tubular or spiral  
15 wound forms; suitable materials are, for example, a porous metal, ceramic, cermet, glass, mineral, carbon or polymer. Typical metals include stainless steels, Inconel, Hastalloy, Fecralloy, chromium and titanium. The metal may be in the form of a fibrous mesh (e.g. Bekipor filters), a combination of fibrous metal with sintered metal  
20 particles (e.g. Pall PMM metal filter and Supramesh filter), or sintered metal filters (e.g. Pall PSS filter media). Woven metal filter media may also be used. Inconel, Hastalloy, Fecralloy, Bekipor, Pall and Supramesh are Trade Marks.

Typical polymeric substances include any type of filtration  
25 media including woven and non-woven media. These may optionally be coated with metal or metal oxide films.

Porous ceramic, glass, carbon or mineral media may be used including porous carbons, silicon carbide, porous clays or other silicate minerals, e.g. kaolin, vermiculite, montmorillonite and  
30 pillared clays, aerogels or supported aerogels and supported porous silica. The support may itself be a zeolite, formed into a suitable shape using a binder. By choice of a suitable support, very robust membranes may be produced. The use of metal supports is especially preferred.

35 The pore size of the support is an important parameter. Many

prior art membranes have used supports with very small pore sizes. A major advantage of the present invention compared with published prior art is that it enables a support with a large pore size to be used. In particular, the pore diameter can be larger than the average crystal size of the zeo-type material. Large pores are advantageous because they permit the preparation of high surface area membranes, and thus maximise flux. Preferably, the average pore diameter of a support used in the present invention is in the range of from 0.1 to 2000 microns, preferably 1 to 2000 microns, especially 5 to 200 microns. For pores of up to 300 microns diameter, the pore size may be determined by the technique of bubble point pressure as defined by ISO4003, and the pore size distribution may be measured by a Coulter porometer (Trade Mark). For larger pores, optical microscopy methods may be used.

In an especially preferred embodiment of the invention, the surface of the support which is immersed in a solution or suspension containing a source of silicic acid and subsequently in a synthesis gel which is capable of crystallising to produce a crystalline zeo-type material, incorporates a surface coating of nickel, cobalt or molybdenum in the form of the metal and/or the oxide. This surface coating incorporated in the support will normally be predominantly in the form of the oxide, as nickel, cobalt or molybdenum tend to oxidise in air. The use of molybdenum or, especially, cobalt, is preferred.

The surface coating may be deposited by any suitable method, for example by vacuum evaporation, vapour deposition, Rf sputtering or electroplating. It may also be deposited by soaking the support in a solution of a salt of the relevant metal followed by firing in air to oxidise the deposited layer. Where a technique results in the deposition of nickel, cobalt or molybdenum metal, this initial deposit may if desired be converted to give a thick layer of the oxide by heating in a stream of oxidising gas, conveniently air.

The synthesis gel used in step iii) of the process of the present invention may be any gel which is capable of producing the desired crystalline zeo-type material. Gels for the synthesis of

zeo-type materials are well known, and are described in the prior art given above or, for example, in EP-A-57049, EP-A-104800, EP-A-2899 and EP-A-2900. Standard text books by D W Breck ("Zeolite Molecular Sieves, Structure Chemistry and Use", published by John Wiley, 1974) and P A Jacobs and J A Martens (Studies in Surface Science and Catalysis, No. 33, "Synthesis of High Silica Aluminosilicate Zeolites", published by Elsevier, 1987) describe many such synthesis gels. The process according to the present invention includes conventional syntheses of zeo-type materials, except that the synthesis is carried out in the presence of the porous support. Most commonly, gels are crystallised by the application of heat. Pressure may also be applied, but it is usually convenient to conduct the crystallisation under autogenous pressure. The optimum time for the crystallization step (iii) depends on the nature of the gel and the temperature, which may be 20°C to 220°C, but especially 60-120°C. In general the time may be in the range 3-200 hr, in particular 4-150 hr with higher temperatures needing lower times; crystallization times of at least 8 hr, especially at 80-100°C, e.g. 8 hr to 5 days, in particular 10-80, especially 10-30 hr are preferred.

In our European patent application No. 91309239, where zeo-type crystals are deposited on a support by a process equivalent to step iii) of the process of the present invention without steps i) and ii) being carried out, a single immersion and crystallisation step produces some crystals on the surface of the support, but these crystals may not be sufficient to produce a continuous crystal growth over the whole surface, and a second immersion and crystallisation step is necessary. After the support has been subjected to a second crystallisation, more crystals have been grown, either directly from the surface of the support or from the surface of the crystals formed in the first crystallisation which have themselves directly grown on the support surface. The process of immersion and crystallisation may be repeated as required, preferably until a complete and continuous coverage of the support surface is obtained. In the process of the present invention, a

much greater coverage of crystals is obtained after carrying out a single immersion and crystallisation step iii) following the steps i) and ii) than is obtained without steps i) and ii). Under suitable conditions, it may sometimes be possible to obtain a  
5 finished membrane with a single immersion and crystallisation step iii). It may however still be necessary to repeat the immersion and crystallisation step iii) more than once to obtain the required coverage. Accordingly, the invention also provides a process for the preparation of a membrane which comprises a process according to  
10 the invention, characterised in that, after crystallisation of the initial gel according to step iii), the support is removed from the mix, and the contact, e.g. immersion and crystallisation of step iii) are repeated one or more times to obtain the required membrane.

The number of contacts, e.g. immersions and crystallisations  
15 according to step iii) required will of course depend on the nature of and the pore size of the support, the nature of the zeo-type material and the synthesis conditions; for example, up to 10, especially up to 4, immersions may be desirable. The use of the process of the present invention increases the initial coverage of  
20 zeo-type material and hence reduces the total number of contacts required to make a finished membrane. In addition, the process according to the invention leads to a finished membrane which is in general thinner than the membranes prepared by other methods. This in turn improves the flux through the membrane.

25 Preferably, after removal of the support from the mixture after step iii), loose material is removed, for example by thorough washing, before carrying out any subsequent contact and crystallisation steps iii). The support may also be dried between each immersion. Drying for at least 12 hours at ambient  
30 temperature, at a temperature of 30-50°C for at least 2 hours, or at a temperature of 80-100°C for 15 to 30 minutes, are suitable regimes.

The finished membranes claimed in our European application No. 91309239 and which can be produced by the process of the present  
35 invention, have two distinct characteristics. First, the zeo-type

material is in direct contact with the surface of the support and directly bonds thereto. The nature of the bonding is not fully understood; it may be primarily chemical bonding and/or physical bonding, but in either event the crystals form directly from the support surface without any intermediate "glue" or binder. This is distinct from prior art membranes, for example those described in EP-A-180200, where pre-formed crystals of zeolite are brought together with the pores of a support and, in effect, glued or cemented in position. In the finished membranes of our copending application, crystal growth begins at the support surface, and continues outwards continuously, until it cross-links with the crystals growing from the opposite sides of the pores of the support and forms an essentially continuous film of zeo-type material.

Secondly, the zeo-type material presents an essentially continuous crystal growth, each individual crystal growing out from the surface of the support or from the surface of adjacent crystals. This is, again, distinct from prior art membranes where pre-formed crystals are brought into intimate contact and "glued" together, or where coverage of the surface of a support is incomplete. There is no intermediate layer of amorphous material between the support and the crystal growth.

In these membranes, the growth of zeo-type material is essentially continuous over the pores of the support. Preferably, it is essentially continuous over the whole surface of the support. In this case, the layer of zeo-type material may for example be 100 microns thick or even thicker; it may for example be from 1 to 100 microns, especially from 1 to 70 microns, thick. As well as providing a covering over the pores of the support, the growth of zeo-type material may if desired extend through the pores, into the body of the support.

Preferably the crystal growth in a membrane produced by the process of the invention is completely free from pin-holes. In reality, of course, it may be difficult to produce a perfect membrane, and the term "essentially continuous" is intended to include membranes having a small number of pin-holes in the crystal

growth. When membranes are prepared using a crystallisation method, such pin-holes are fissures formed when the faces of growing crystals do not match up exactly. Such-pin holes may be present immediately after preparation of the membrane, but are also likely to occur after dehydration or ion-exchange of the membrane, or during the working life of the membrane. The membranes are clearly distinct from prior art membranes where the crystal growth has major discontinuities, the growth resulting in macro-pores.

Minor quantities of pin-holes in the membrane can be blocked using a suitable post-treatment, for example using an organic material, for example a polymer or an organo silicon material, or an inorganic material, for example an inorganic silicon material, capable of cross-linking with silicon and oxygen atoms.

The essentially continuous crystal growth in the finished membranes, supplemented if necessary by a post-treatment, is such that there is no access from one side of the membrane to the other except through the intra-crystalline pores of the zeo-type material.

The finished membranes made by a process incorporating the present invention have a wide range of applications. They may for example be used for dehydration, for example to remove water from materials such as LPG, natural gas or alcohols. Such membranes are very much more effective than the traditionally used organic polymer membranes, for example the commercially available caesium polyacrylate membranes described in WO 86/00819, in dehydrating mixtures of water with other liquids; they have the additional advantage of being useful at relatively high temperatures.

They may be used for removing linear alkanes, olefins or other functionalised hydrocarbons from a mixture containing more highly branched compounds, for example in the octane-enhancing of fuels, reforming, dewaxing, or the separation of normal and iso butanes.

Combined catalysis and separation processes are another important application. Examples include hydrogenation and dehydrogenation of linear hydrocarbons in the presence of more highly branched compounds such as isoalkanes, isoalkenes and aromatics. The membranes may be used in catalysis to shift

thermodynamic equilibria towards the desired product, for example by removal of hydrogen from a dehydrogenation reaction or removal of water from an esterification reaction or an alcohol dehydrogenation.

The following Examples illustrate the invention.

5       The chemicals used in the Examples are:-

Sodium Aluminate : ex BDH Technical grade nominally containing 40%  $\text{Al}_2\text{O}_3$ , 30%  $\text{Na}_2\text{O}$  and 30%  $\text{H}_2\text{O}$

Sodium Silicate : ex BDH specific gravity 1.57

Example 1

10   Preparation of Membranes

The substrate used was a 3 x 3 x 1 cm block of a multi-channel membrane available under the Trade Mark "Membralox" SCT Type Z. This substrate is composed of alpha-alumina and zirconia, has a pore size of 50 nm, and has 19 channels of 4 mm internal diameter.

15       The block was degreased by soaking it in a beaker containing approximately 200 ml of toluene for 1 hour (liquor being replaced 3 times). The toluene was then replaced by acetone and the washing procedure repeated. The block was subsequently air dried by carefully placing it in a clean petri dish, loosely covering with  
20   aluminium foil and placing in a fume cupboard overnight.

The clean, dry block was placed in a QVF (Trade Mark) glass tube (80 cm diameter). The QVF tube was equipped with PTFE end plates which were held in place by stainless steel flanges held in place by metal nuts and bolts. The vessel had previously been  
25   cleaned by washing it with distilled water, acetone, toluene and finally acetone before being dried in a stream of clean, dry air.

Two solutions, A and B, were prepared separately as follows in two 16 oz glass bottles.

Solution A: 34.4 g sodium aluminate (BDH Technical Grade) and 155.0  
30   g distilled, deionised water. The aluminate was analysed with results as follows: 27.44%  $\text{Na}_2\text{O}$ , 43.36%  $\text{Al}_2\text{O}_3$  and 29.20%  $\text{H}_2\text{O}$ .

The mixture was then mechanically shaken until dissolved.

Solution B: 53.4 g sodium silicate specific gravity 1.57 (BDH), analysis gave 13.53%  $\text{Na}_2\text{O}$ , 29.28%  $\text{SiO}_2$  and 57.20%  $\text{H}_2\text{O}$ ; and 155.0 g  
35   distilled, deionised water.

Solution A was added slowly to solution B with both stirring and shaking (by hand) to ensure complete and even mixing (it is important to ensure that no lumps of hydrogel are formed). This resulted in a hydrogel having the nominal molar composition:

5         $2.0\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.0\text{SiO}_2:143\text{H}_2\text{O}$

The molar composition based on the analysis figures above was:

1.83  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:1.78 \text{SiO}_2:132.9 \text{H}_2\text{O}$

The hydrogel was slowly poured into the QVF tube containing the block. The tube was sealed with the second PTFE disc and metal end flanges and placed in an oven pre-heated to 90° for 2 hours. Subsequently it was removed and cooled quickly in iced water for 5-10 minutes. The tube was opened at one end and the solution poured away whilst the block was carefully removed with a long flat rod ensuring that the block was not damaged in any way. The block was placed in a glass beaker and washed three times with 100 ml aliquots of distilled, deionised water, swirling the solution each time to ensure complete removal of residual zeolite solution. It was then dried in an oven at 90°C for 20 minutes, and wiped with a tissue to remove residual material. This washing and drying was then repeated.

A fresh hydrogel was then made using fresh solutions A and B as above. The mesh was immersed in the fresh hydrogel, and the immersion and washing was repeated as above except that the duration of the immersion was 24 hours instead of 2 hours.

25        Examination of the surface of the block by scanning electron microscopy (SEM) showed a significant number of cubic zeolite A crystals bonded directly to the surface of the block.

#### Example 2 (Comparative)

The procedure of Example 2 was repeated exactly except that the initial immersion step (2 hours at 90°C) and subsequent washing was omitted. Examination of the resulting block by SEM showed a much inferior coverage of zeolite.

#### Example 3

The procedure of Example 1 was repeated exactly except that, before the initial immersion step, the block was provided with a



surface coating containing cobalt.

The support was immersed in 500 mls of 0.1 M  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  for 2 hrs at room temperature. The support was then removed and put in a glass petri dish and a layer of fresh 0.1 M  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution was pipetted onto the surface. The support was dried for 30 minutes at 90°C and a second aliquot was applied. The support was dried at 90°C for 90 minutes, and then heated in air at 550°C for 6 hours.

The resulting block was subjected to the procedure of Example 1 and then examined by SEM. It had a continuous surface coating of zeolite crystals: an SEM, magnification x 500, is shown in Figure 1.

Example 4

The substrate used was a Bekipor (Trade Mark) ST5BL3 filter. This consists of very fine 316 stainless steel fibres brought together in a 3-dimensional labyrinthic structure. The fibres are arranged randomly into a homogeneous web. This web is further compacted and sintered to give a very strong metallic bond at each fibre crossing. The average pore size measured by Coulter porometer is 5.3 microns and the diameter of the wires on the top surface is 6.5 microns.

A 7 cm disc of this mesh was degreased as described in Example 1. It was then immersed in a solution of 53.4 g sodium silicate in 155 g water at 90°C for 4 hours. After removal, the mesh was washed thoroughly with water, and then immersed in a hydrogel prepared from solutions A and B as described in Example 1. Subsequent treatment was as in Example 1.

Visual examination by SEM showed approximately 30% coverage of the pores of the support.

In a comparative experiment, the sodium silicate immersion step was omitted. Visual examination of the finished mesh showed approximately 20-25% coverage of the pores of the support.

Example 5

The general procedure of Example 1 was repeated using the substrate defined in Example 4; immersion in the initial hydrogel was for 5 minutes at 90°C. After removal from the initial hydrogel and washing, the mesh was analysed using transmission electron

microscopy and X-ray analysis.'

A transmission electron micrograph magnification x 100,000 is shown in Figure 2. Hemispherical globules are shown bonded directly to the surface. The X-ray analysis showed these globules to contain  
5 predominantly silicon and oxygen. These globules are silicic acid oligomers.

10

15

20

25

30

35

## Claims:

1. A process for the deposition of a zeo-type material on a porous support, which comprises the following steps: i) contacting at least one surface of the porous support with a solution or suspension containing a source of silicic acid, under conditions such that  
5 oligomers of silicic acid become bonded directly to said surface of the support; ii) separating the support with said oligomers bonded thereto and said solution or suspension containing a source of silicic acid; and iii) subsequently contacting said surface of the support with a synthesis gel which is capable of crystallising to  
10 produce a crystalline zeo-type material, and inducing crystallisation of said gel so that zeo-type material crystallises on said surface.
2. A process according to claim 1 characterised in that step (i) comprises immersing said surface in said solution or suspension,  
15 step (ii) comprises removing said support from said solution or suspension and step (iii) comprises immersing said surface in said gel.
3. A process according to claim 1 or 2 characterised in that between steps (ii) and (iii) the support with said oligomers bonded  
20 thereto is washed to remove said solution or suspension and any loose material.
4. A process according to any one of the preceding claims characterised in that in step (i) the surface is immersed in a synthesis gel, which is capable of crystallizing to produce a  
25 crystalline zeo-type material, for a period of time sufficient to

bond said oligomers to said surface.

5. A process according to claim 4 characterised in that the immersion step (iii) is into a fresh synthesis gel.

6. A process according to any one of the preceding claims  
5 characterised in that the porous support before step (i) incorporates a surface coating of nickel, cobalt and/or molybdenum, in the form of the metal and/or its oxide.

10

15

20

25

30

35

1/1

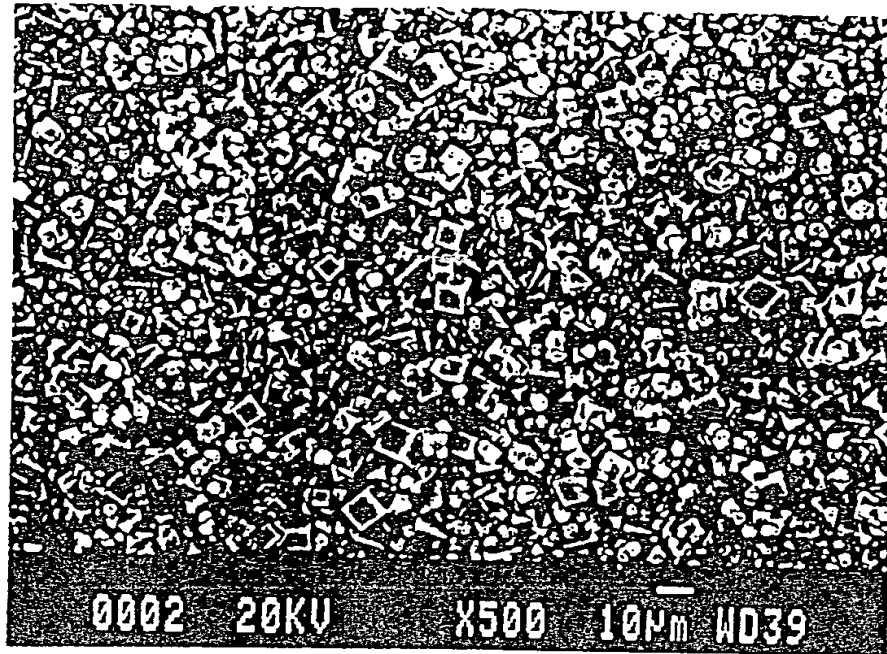


FIG. 1

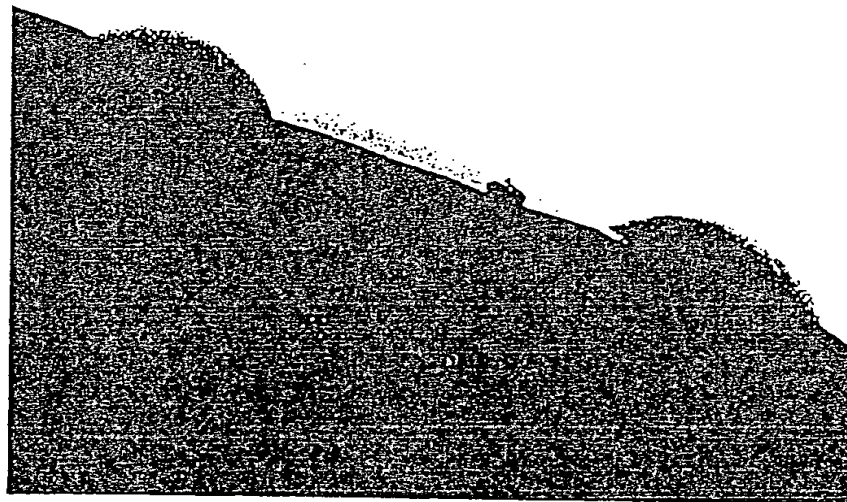


FIG. 2

SUBSTITUTE SHEET

# INTERNATIONAL SEARCH REPORT

1

International application No.

PCT/GB 93/00627

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01D 71/02, B01D 69/10, B01J 29/00  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS-ONLINE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--|-----------------------|
| X,P       | EP, A1, 0481660 (THE BRITISH PETROLEUM COMPANY P.L.C.), 22 April 1992 (22.04.92)<br>--   | 1-6                   |
| X,P       | EP, A1, 0481659 (THE BRITISH PETROLEUM COMPANY P.L.C.), 22 April 1992 (22.04.92)<br>--   | 1-6                   |
| X         | US, A, 4699892 (H. SUZUKI), 13 October 1987 (13.10.87), claim 10, see examples 9, 10<br>--   | 1-6                   |
| X         | PATENT ABSTRACTS OF JAPAN, vol. 13, no. 119 (C-579) /3467/, 23rd March 1989; & JP - A - 63 291809 (IDEMITSU KOSAN CO LTD) 29-11-1988<br>-- | 1-6                   |

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

- \* Special categories of cited documents:
- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

- \* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \* "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \* "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \* "&" document member of the same patent family

Date of the actual completion of the international search

28 June 1993

Date of mailing of the international search report

29.07.93

Name and mailing address of the ISA/

European Patent Office, P.O. 5818 Patentplatz 2  
NL-2280 HV Rijswijk  
Tel.: (+31-70) 340-2040, Tx 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

GÖRAN KARLSSON

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 93/00627

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages        | Relevant to claim No. |
|-----------|---|-----------------------|
| X         | DE, A, 3827049 (SCHULTEN, R.), 15 February 1990<br>(15.02.90)<br><br>--                   | 1-6                   |
| A         | EP, A2, 0180200 (SUZUKI, HIROSHI), 7 May 1986<br>(07.05.86)<br><br>--                     | 1-6                   |
| A         | CA, A, 1235684 (SAKURADA, SATOSHI ET AL.),<br>26 April 1988 (26.04.88)<br><br>--<br>----- | 1-6                   |

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

No. '2065

28/05/93

International application No.

PCT/GB 93/00627

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)      | Publication<br>date  |
|---|---------------------|---------------------------------|----------------------|
| EP-A1- 0481660                            | 22/04/92            | AU-A- 8473991<br>JP-A- 5043218  | 30/04/92<br>23/02/93 |
| EP-A1- 0481659                            | 22/04/92            | AU-A- 8472691<br>JP-A- 5043219  | 30/04/92<br>23/02/93 |
| US-A- 4699892                             | 13/10/87            | EP-A- 0135069<br>JP-A- 60028826 | 27/03/85<br>14/02/85 |
| DE- A- 3827049                            | 15/02/90            | NONE                            |                      |
| EP-A2- 0180200                            | 07/05/86            | JP-A- 61107902                  | 26/05/86             |
| CA-A- 1235684                             | 26/04/88            | NONE                            |                      |